Short communication

Nonflammable electrolyte for rechargeable lithium battery with sulfur based composite cathode materials

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HIGHLIGHTS

► Safety of Li/S battery has been improved via using nonflammable electrolyte.
► Dimethyl methylphosphonate (DMMP) obviously restrains the flammability of EC-DMC carbonate electrolytes.
► Addition of DMMP in the range of 7–11 wt.% makes electrolyte nonflammable and Li/S battery demonstrates stable cycling and good power rate performances.

ARTICLE INFO

ABSTRACT

The concept of improving the safety of rechargeable lithium sulfur batteries by introducing flame retardant additives (FRs) to liquid electrolytes is primarily reported in this paper. Dimethyl methylphosphonate (DMMP) is used as a flame retardant additive to improve the thermal safety of rechargeable lithium batteries with sulfur based composite cathode materials. The electrochemical compatibility between DMMP and sulfur cathode is investigated. With 11 wt.% DMMP addition, the electrolyte of 1 M $LiPF_6$/EC+EMC (1:1, v/v) is nearly nonflammable and its thermal stability is obviously improved. Cycle performance and electrochemical stability are little affected with an appropriate DMMP addition of 7–11 wt.% by the analysis of electrochemical impedance spectra (EIS) and cycle performances. DMMP is a feasible choice as flame retardant additive in carbonate electrolyte for rechargeable lithium batteries with sulfur composite cathode materials.

1. Introduction

In the recent years, tremendous efforts have been made to extend the application of lithium ion batteries to the fields of electric or hybrid vehicles and energy storage devices [1]. However, safety problems and low energy density of ~150 Wh kg^{-1} have held back the large-scale application of lithium ion batteries employing organic liquid electrolytes which are highly flammable. Lithium sulfur batteries with a remarkable theoretical energy density 2567 Wh kg^{-1} and high specific capacity 1672 mAh g^{-1} for elemental sulfur cathode materials can dramatically increase the energy density of batteries which are aimed to be used in the field of hybrid vehicles and energy storages [2]. Unlike the insertion chemistry of conventional lithium sulfur batteries, lithium sulfur batteries build an innovative "integration chemistry" that tolerates

charges or discharges, reducing overcharge dangers that often happen to lithium ion batteries [3]. In our previous studies, high reversible specific capacity and stable cycle performance have been achieved in polyacrylonitrile (PAN) and sulfur composite cathode based rechargeable lithium batteries [4–8], in which commercialized electrolyte of 1 M $LiPF_6$/EC+EMC (1:1, v/v) was used in cell fabrication, while some studies on lithium sulfur batteries employ much more volatile and flammable ether solvents such as 1,3-dioxolane (DOL) and dimethyl ether (DME) with low boiling points (75–85 °C) [9–12]. Even though lithium sulfur batteries have the advantage of high energy density, the safety concerns cannot be ignored because lithium sulfur batteries may undergo the same thermal runaway problems as lithium ion batteries [13]. Possible reasons are as follows: (1) the formation of lithium dendrite and high reactivity of metal lithium with organic solvent may cause hazards [1]; (2) the mixtures of conductive carbon material and sulfur are very unsafe as they are inflammable and explosive materials, where the carbon component is often utilized to enhance

the conductivity of cathode materials; (3) high volatility and flammability of carbonate or ether solvent are thermally unstable and easy to be ignited, probably resulting in fire or even explosion of batteries.

Given the extensive usage of lithium sulfur batteries as large size, strategies must be taken to enhance its safety. Little information about inner or outer protection of lithium sulfur batteries has been reported so far. One economical method is adding fire retardant solvents into organic electrolytes as co-solvents or additives. The most explored fire retardant additives in lithium ion battery electrolytes include alkyl phosphate [14–19], fluorinated alkyl phosphate [20,21], ionic liquid [22], phosphazene [13]. Promising results have been reported for dimethyl methyl phosphonate (DMMP) either as an additive or a pure solvent in promoting the nonflammability with small impact on the performances of lithium ion batteries [15,23,24].

DMMP has moderate viscosity (1.75 mPa s), high dielectric constant (22.3) and high boiling point (180 °C) [24]. Moreover, with high phosphorus (P) content (25 wt.%), the flame retarding efficiency of DMMP is better than other kinds of FRs with a relatively lower amount of addition. Taking all above into consideration, DMMP was chosen as FR additive in rechargeable lithium batteries with sulfur composite materials. In this work, the flame resistance of electrolytes with different DMMP additions and the correlation between DMMP amount and electrochemical characteristics of batteries were investigated together with cycle performance and rate capability tests.

2. Experimental

2.1. Composite material preparation

PAN (1 g) and 8 g sulfur were mixed homogeneously by ball milling for 12 h with ethanol as a dispersant. The pale yellow powder was collected after drying, then heated at 300 °C for 200 min in N_2 atmosphere, resulting in black powder PAN/S composite with sulfur content ca. 50 wt.%, which was determined by elemental analysis via PE 2400 II, Perkin Elmer.

2.2. Coin-cell assembly and electrochemical performance measurements

The cathode was fabricated by mixing 70 wt.% PAN/S composite, 20 wt.% Super P and 10 wt.% PTFE as binder, and distilled water as dispersant. The slurry was stirred for 4 h and then uniformly coated onto a thin Al foil (with a carbon coating), dried and cut into small disks with weight loads of ca. 0.5–2 mg cm^{-2}. The 1 M LiPF$_6$/EC+EMC (1:1, v/v) was used as baseline electrolyte, in which DMMP was directly added at the ratios of 0, 7, 11, 15, 21 wt.%. With lithium foil as anode and PE film as separator, 2016 type coin cells were assembled in a glove box (MBraun, Germany).

2.3. Flame resistance, conductivity and thermal stability measurements

Self-extinguishing (SET) time was chose to evaluate the flammability of electrolytes. A cotton ball-wick was immersed in the as-prepared electrolyte to absorb 0.2–0.3 g liquid, then it was ignited in a fume hood and the time for the flame to extinguish was recorded [15]. The results were normalized against the electrolyte mass and the SET tests were repeated at least six times.

The ionic conductivities of electrolytes with different DMMP contents were measured at room temperature via the FE30 conductivity meter and the Inlab 710 conductivity measuring cell (Mettler Toledo, Switzerland).

The electrolytes alone and in the presence of full charged electrode material were sealed in aluminum pans and their thermal stability was determined by differential scanning calorimeter (DSC) via NETSCH STA 449 at a heating rate of 10 °C/min from 30 °C to 300 °C in Ar. A pinhole was punched on the pan before DCS measurement.

2.4. Electrochemical performance

The charge/discharge performances of coin cells were conducted on a LAND cycler (Wuhan, China), and electrochemical impedance spectra (EIS) were tested on the cells after second cycle with a CHI604D Electrochemical Workstation. The frequency ranged from 10 kHz to 0.01 Hz and the amplitude was set at 5 mV. All the experiments were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the effect of DMMP content on both self-extinguishing time and ionic conductivity. With 7 wt.% DMMP added, the SET of the electrolyte dramatically decreases from 104.08 s g^{-1} of baseline electrolyte to 37.41 s g^{-1}. The electrolyte becomes nonflammable when the content of DMMP increases to 11 wt.% or higher, as suggested by an SET near zero. Such a small amount of DMMP can effectively retard the flame of the electrolytes. The most accepted explanation for the suppression of flame is the "free radical capture mechanism" [14,19]. That is, DMMP captures the free radicals emitted from the burning of electrolytes, forming nonflammable phosphoric acid and mitigating or inhibiting flaming chain reactions. On the other hand, the conductivity of electrolytes reaches a maximum at 7 wt.% (11.89 mS cm^{-1}) implying that a proper amount of DMMP may improve the ionic conductivity of the electrolyte by diminishing the lithium ion solvation radius because DMMP has relatively high dielectric constant of 22.3. When the DMMP amount increases to 15 wt.%, the conductivity curve exhibits a declining tendency. As the decline in conductivity is not so notable, it can be attributed to the slight decrease in the concentration of lithium salt and increase in the electrolyte viscosity because of DMMP's high viscosity (1.73). Regardless of the slight reduction of conductivity, 11–15 wt.% DMMP is enough for effectively retarding the flame of carbonate electrolytes.
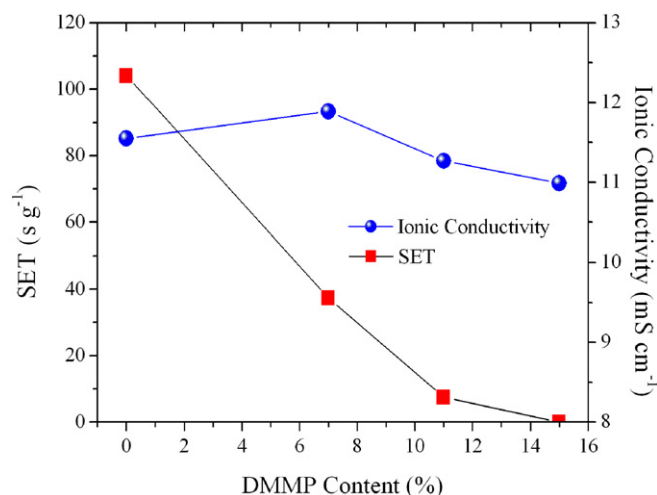

Fig. 1. SETs and ionic conductivities of the electrolyte 1 M LiPF$_6$/EC+EMC (1:1, v/v) with different DMMP contents.

Fig. 2 compares the thermal stability of electrolytes without and with 11 wt.% DMMP. The first reaction peak of normal electrolyte is observed at 150 °C, while no apparent peaks are observed in the same temperature range for the DMMP-added electrolyte. And strong exothermic peaks for both electrolytes are 266 °C and 270 °C, respectively. These results indicate that DMMP can strengthen the thermal stability of the electrolyte. The thermal stability of DMMP-added electrolyte in the presence of fully charged sulfur composite based electrode was also investigated, as shown in. Fig. 2c. There is an exothermic peak at lower temperature compared to Fig. 2b. PAN/S composite was prepared at 300 °C [8], and it alone is thermally stable before 300 °C. That is to say, the exothermic peak might also be affected by the possible reaction between PAN/S electrode with electrolyte at high temperature.

Charge and discharge behaviors of coin cells assembled with different amounts of DMMP are shown in Fig. 3a. The first discharge capacities within a range of 850—910 mAh g^{-1} are not given in the figure as the present work mainly focuses on the influence of DMMP additive on the reversible capacities of the cells. All specific capacities presented in this work are calculated on the basis of whole composite mass except for special notation. The theoretical specific capacity of the sulfur composite material is 836 mAh g^{-1} calculated via multiplying 1672 mAh g^{-1} by sulfur content of 50 wt.%. With only 7 wt.% DMMP added, the voltage gap between charge and discharge curves remains unchanged and a high initial reversible capacity 723 mAh g^{-1} calculated on whole composite mass is obtained. Considering pure sulfur, the specific capacity is 1446 mAh g^{-1} with 86% sulfur utilization (1446 mAh g^{-1} divided by sulfur theoretical specific capacity 1672 mAh g^{-1}). When the amount of DMMP increases to 11 wt.%, a specific capacity of 728 mAh g^{-1} is achieved as the discharge voltage plateau descends slightly. The polarization during both charge and discharge processes enlarges as there existed obvious voltage gaps in charge/discharge curves of the cells with the electrolytes containing 15 wt.% and 21 wt.% DMMP, indicating that excessive DMMP affects the interface resistances of electrode/electrolyte. EIS measurements of the cells after the second cycle are displayed in Fig. 3b. Each Nyquest plot shows a semicircle in the high frequency that represents charge transfer resistance (R_{ct}) between the electrode and the electrolyte. The R_{ct} values of the cells are 59.4 Ω, 48.6 Ω, 100.5 Ω, 229.9 Ω and 476.6 Ω with the electrolytes containing DMMP from
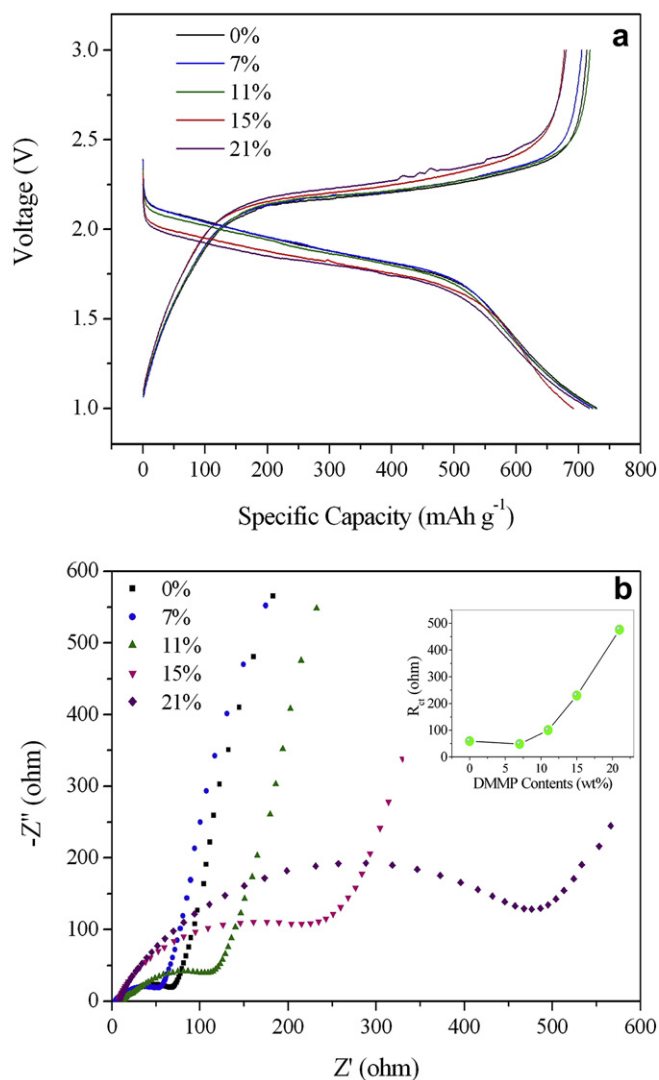

Fig. 3. (a) Charge/discharge profiles and (b) impedance spectra of the cells with the electrolytes containing 0—21 wt.% DMMP in second cycle at 0.1C. (Insert) Charge transfer resistances as a function of DMMP contents.

0 to 21 wt.%, respectively, as shown in the insert of Fig. 3b. These data prove that DMMP addition does significantly impair the interface resistances of the cells. Generally, higher DMMP contents, bigger R_{ct}. However, 7 wt.% DMMP adversely reduces the charge transfer resistance, suggesting enhanced electrochemical kinetics. As discussed before, 7 wt.% DMMP may contribute to reducing the lithium ion solvation radius, which not only improves the ion conductivity but also facilitates the lithium ion transport in the pores of nano-sized composite and accelerates the electrode reaction process. When the DMMP amount exceeds 11 wt.%, the R_{ct} increases sharply, corresponding with the larger polarized voltage in charge/discharge curves in Fig. 3a. Lithium metal with fresh surface will slowly react with DMMP, and reduces DMMP to form a black passivated film on lithium sheet surface. Feng et al., have used DMMP as pure nonflammable electrolyte for LiMn$_2$O$_4$/Li half cells and stable cycle performance was obtained [23]. However, the lithium cells with PAN/S composite cathode failed to cycle even for twice with pure DMMP as solvent and LiClO$_4$ as lithium salt. Whether DMMP had some interactions with sulfur composite electrode or not needs further investigations. All these factors mentioned here could cause unfavorable effects on electrochemical performances and restrict the large addition of DMMP into the
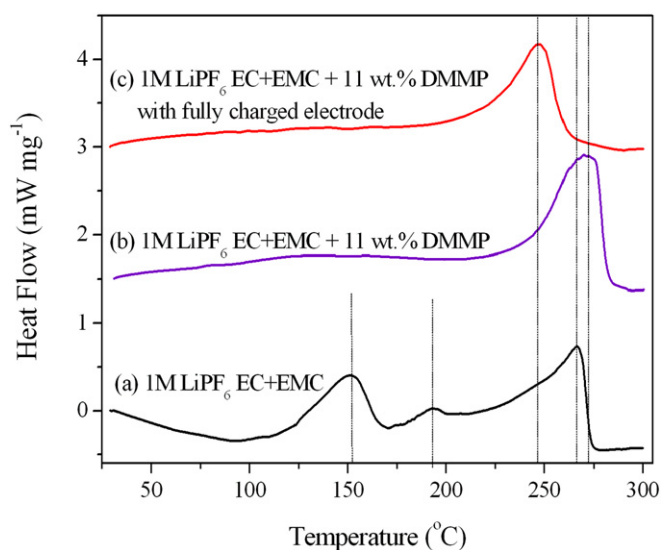

Fig. 2. DSC profiles of (a) 1 M LiPF$_6$/EC+EMC (1:1, v/v) and (b) with DMMP additive and (c) electrolyte containing DMMP with fully charged electrodes.
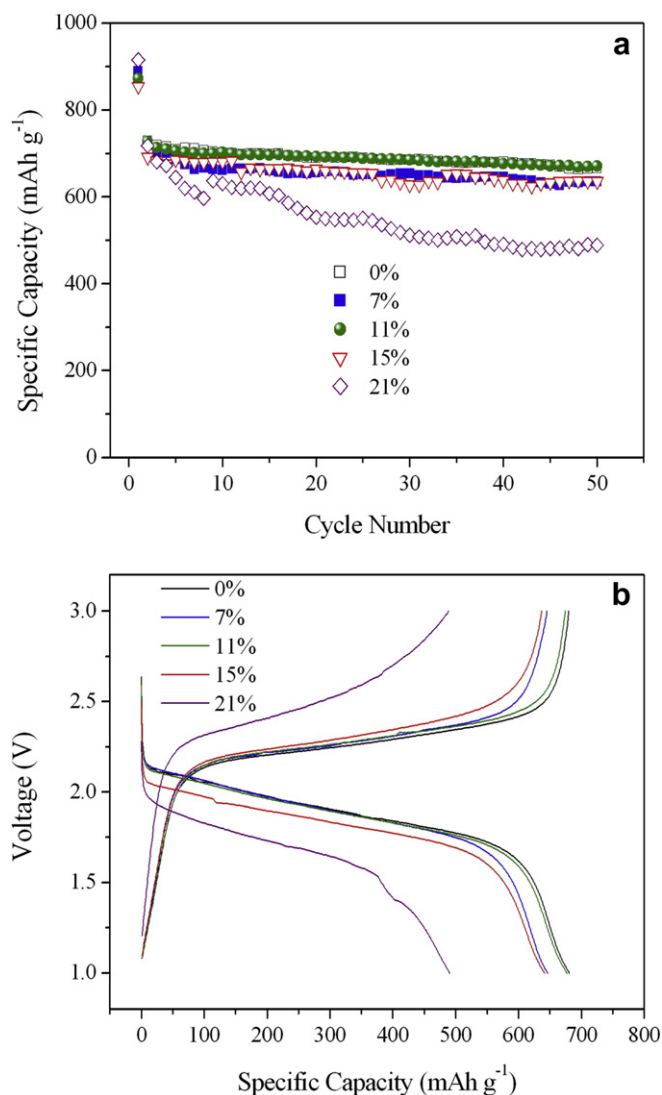
Fig. 4. (a) Cycle performances and (b) charge/discharge profiles of the cells with electrolytes containing 0–21 wt.% DMMP in 40th cycle at 0.1C.

Fig. 5. Rate performances of the cells without and with DMMP additive.

After cycling at 3C rate for several times, both of them preserve a stable capacity of ca. 467 mAh g^{-1} and capacity retention close to 73%, implying that the addition of DMMP no exceeding 11 wt.% has ignorable impact on the high rate performances of the cells, however, bring obvious advantages of electrolyte to be nonflammable.

4. Conclusions

The flammability of sulfur cathode and organic electrolytes, high activity of lithium metal anode as well, determine lithium sulfur batteries possessing high risk of catching fire or even explosion. In this work, nonflammable electrolytes were applied in the rechargeable lithium batteries with sulfur composite cathode materials. The method lies in adding DMMP into the carbonate electrolyte as flame retardant. The effects of DMMP on flame retard, thermal stability and electrochemical properties of the batteries were investigated. The results demonstrate that DMMP addition can significantly suppress the flammability and improve the thermal stability of the commercialized electrolyte 1M LiPF$_6$/ EC+EMC. Meanwhile, with optimized content of DMMP (7~11 wt.%), the batteries with nonflammable electrolyte demonstrate outstanding electrochemical performances, that is, stable cycling and good high power rates. Therefore, DMMP is a suitable flame retardant additive to enhance the safety of rechargeable lithium batteries with sulfur composite cathode materials.

Acknowledgments

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electrolyte. Therefore, 7–11 wt.% DMMP is an optimized addition into the electrolytes at the balance of nonflammability and electrochemical performances.

Cycle performances of cells consist of PAN/S composite and electrolytes containing DMMP are shown in Fig. 4a. The high first discharge capacities ranging from 850 to 910 mAh g^{-1} have exceeded its theoretical capacities ca. 836 mAh g^{-1}, which can be distinctly observed from the picture. One convincible explication is that the conjugated backbone of conductive polymer derived from the reaction between PAN and S contributes to the additional capacity [25]. Stable cycle performances have been obtained when the concentration of DMMP are confined within 11 wt.%. While the cells with 15 wt.% DMMP-containing electrolytes cycled also stably, the relatively higher polarized voltage gaps cannot be ignored (Fig. 4b). For cells containing 21 wt.% DMMP-electrolyte, capacity fades fast due to a retarded electrochemical reaction process involving a large cell impedance.

Rate performances of cells without or with 11 wt.% DMMP additive were also tested, as shown in Fig. 5 at various discharge rates, namely, 0.2C, 0.5C, 1C, 2C and 3C with the same charge rate of 0.2C. There is no distinct difference between the two kinds of cells.
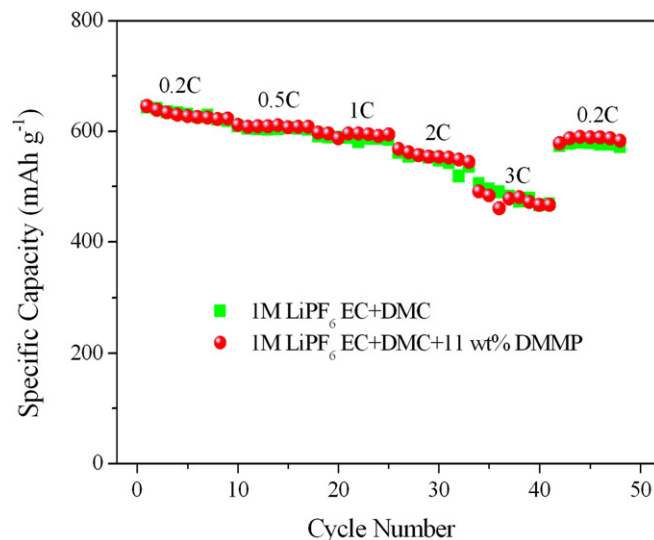
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